

INFLUENCE OF BOEHMITE PRECURSOR ON ALUMINOSILICATE AEROGEL PORE STRUCTURE, PHASE STABILITY AND RESISTANCE TO DENSIFICATION AT HIGH TEMPERATURES

Frances I. Hurwitz, Haiquan Guo, Katy N. Newlin

NASA Glenn Research Center
Cleveland, OH 44135
Ohio Aerospace Institute
Cleveland, OH 44135
University of Louisville
Louisville, KY 40292

Introduction

Aluminosilicate aerogels are of interest as constituents of thermal insulation systems for use at temperatures higher than those attainable with silica aerogels. It is anticipated that their effectiveness as thermal insulators will be influenced by their morphology, pore size distribution, physical and skeletal densities. The present study focuses on the synthesis of aluminosilicate aerogel from a variety of Boehmite (precursors as the Al source, and tetraethylorthosilicate (TEOS) as the Si source, and the influence of starting powder on pore structure and thermal stability.

Experimental

Synthesis. Aluminosilicate aerogels were prepared by a method similar to that of Aravind1 at Al:Si ratios of 8Al:1Si and 3Al:1Si using a number of different Boehmite powders which varied in crystallite size. Boehmite (AlOOH) powders designated as P2, P2W, T25, L4 and X-0 were obtained from Sasol North America. The powders were dispersed in nitric acid solution or water, and sonicated using a Misonix 4000 ultrasonic processor with a 419A tip for 2 minutes at 60 percent power. The dispersed Boehmite was combined with a solution of TEOS in 200 proof ethanol that had been hydrolyzed for 60 minutes with a stoichiometric amount of water and catalyzed with nitric acid. The combined sol was poured into polypropylene molds and held at either ambient temperature or 55°C for 24 hours, following which the hydrogels were extracted into 200 proof ethanol, and then supercritically dried using CO₂.

Characterization. Dried gels were characterized by physical measurement to determine shrinkage and physical density. Skeletal density, was determined by helium pycnometry, and nitrogen adsorption/ desorption was used to determine BET surface area and pore size distribution. Chemical bonding structure was characterized by Fourier Transform Infrared spectroscopy (FTIR). Field Emission Scanning Electron Microscopy (FESEM) was performed on uncoated samples to characterize pore morphology. Thermal analysis of the aerogels was conducted using simultaneous Thermogravimetric Analysis and Differential Thermal Analysis (TGA/DTA) in helium to identify phase transitions. X-ray diffraction was used to characterize both the starting Boehmite powders and the aerogels, as well as identify phases in heat-treated samples.

Results and Discussion

Supercritically dried aerogels exhibited typical physical densities of 0.07-0.08 g/cm³. X-0 aerogels showed the highest stiffness, T25 materials the greatest flexibility. Starting powders varied in crystallite size from 4.9 nm to 11.7 nm. Aerogel pore structure and surface area reflected the size of the starting powder, with highest surface areas, smallest pore sizes and highest

Table I: Typical BET Surface Area as a Function of Starting Powder

Starting powder	Crystallite size, nm	BET m ² /g
P2	4.9	344-379
T25	6.9	279
L4	-	165-182
X-0	11.7	160-192

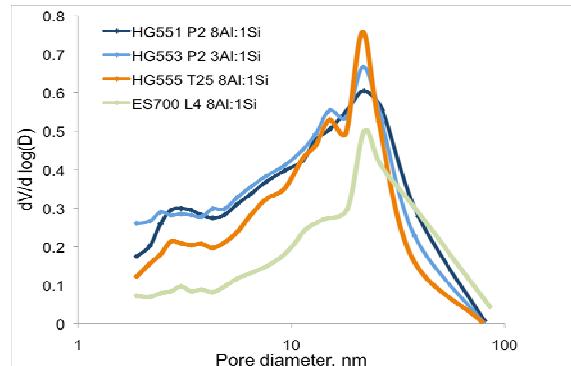


Figure 1. Pore size distribution, as determined by nitrogen desorption.

pore volumes attained from P2 and T25 powders. The relationship between crystallite size and BET surface area is summarized in Table I.

A comparison of nanometer-sized pore size distribution for P2, T25 and L4 derived aerogels, showing a large decrease in the number of small pores and total pore volume, along with a shift to larger pores, in the L4 aerogels, is shown in Figure 1. Characteristic FESEM images, reflecting differences in pore size, pores size distribution, and differences in skeletal morphology of aluminosilicate aerogels from different Boehmite powders are shown in Figure 2.

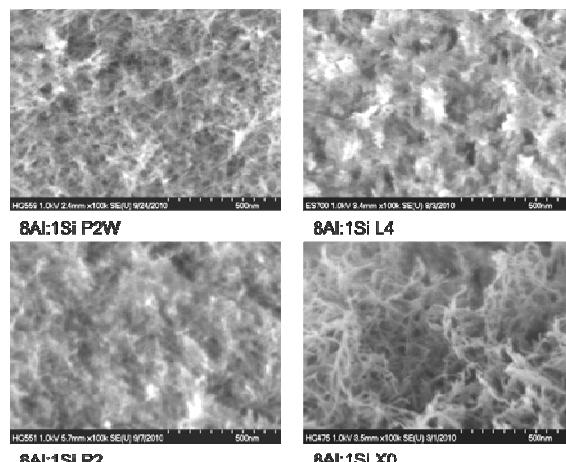


Figure 2. FESEM images show variation in aerogel skeletal structure, pore size and pore volume with choice of starting AlOOH powder.

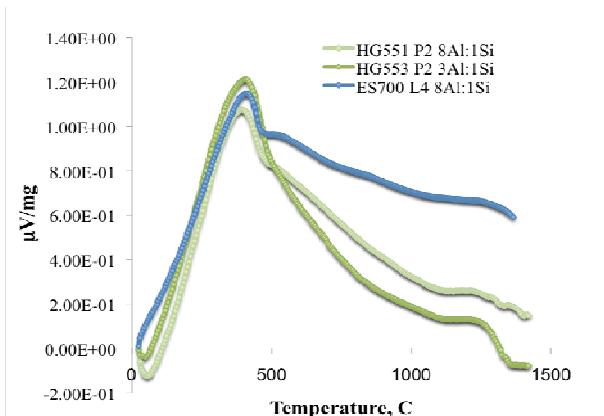


Figure 3. DTA plots of two P2 derived aerogels with 8Al:1Si and 3Al:1Si formulations, and an L4-derived 8Al:1Si aerogel.

The DTA trace in helium acquired at a heating rate of 10°C/m is shown in Figure 3. A characteristic peak in the 385–450°C region is associated with loss of water and accompanying phase transformation from γ -AlOOH to γ -Al₂O₃.² Other transition Al₂O₃ phases also may be present.³ Mass loss ranges from 14 to 23%, depending on the precursor powder, compared with a theoretical mass loss of 15%, based on the reaction



FTIR spectra show more free -OH groups, characterized by an absorbance band at 3400–3350 cm⁻¹, associated with the P2 and T25-derived aerogels than with those synthesized using L4 and X-O. The DTA peak position also shifts with Al:Si ratio, as well as with precursor powder, occurring at higher temperatures, and with less mass change, for aerogels derived from the larger crystallite size materials. Mass loss decreases with larger crystallite size, reflecting differences in associated water with changes in crystallite d-spacing. Higher temperature phase transitions are seen at temperatures >1200°C, and also shift with composition and precursor. These are undergoing further characterization by X-ray Diffraction analysis.

Porous structure is maintained after stepped heating to 900°C, with equilibration at 300, 500, 700 and 900°C. Finer structure is seen in P2 than in L4 gels (Figure 4). Fine pore structure also was maintained in DTA samples in the P2 system following brief exposure to 1425°C (Figure 5).

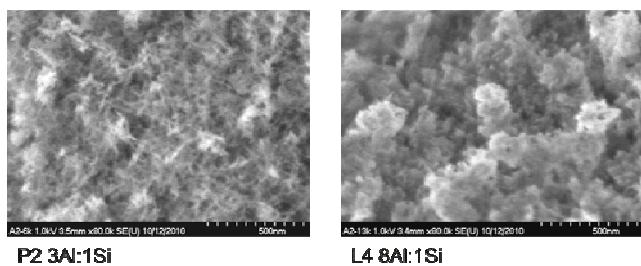


Figure 4. FESEM images of aerogels following stepped heating to 900°C. Finer structure is maintained for P2 aerogels than for L4-derived aerogel.

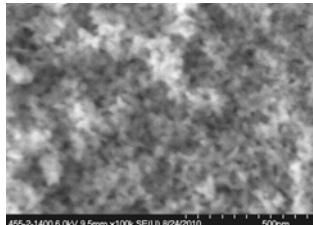


Figure 5. P2 aerogel after heating to 1400°C in He (DTA sample).

Conclusions

Aluminosilicate aerogels have been prepared by the reaction of Boehmite and TEOS in 200 proof ethanol having surface areas of up to 400 m²/g that are capable of maintaining high surface area and fine nanopore structure to temperatures in excess of 1100°C. Pore morphology and the persistence of small pores after high temperature exposure vary with the crystallite size of the Boehmite powder; smaller crystallite size powders lead to higher surface areas and smaller pores, and less coarsening of the microstructure on thermal exposure.

Acknowledgement. The authors wish to thank Anna Palczer and Richard Rogers, Ph.D. and Dereck Johnson, NASA Glenn Research Center, as well as the Hypersonics Project under the NASA Fundamental Aeronautics Program as well as the NASA Radioisotope Power Systems Project for funding.

References

- Aravind, P. R.; Mukundan, P.; Krishna Pillai, P.; Warrier, K. G. K. *Microporous and Mesoporous Materials* **2004**, 96, 14.
- Pecharrromán, C; Sobrados, I.; Iglesias, J. A.; González-Carreño, T.; Sanz, J. *J. Phys. Chem. B*, **1999**, 103, 6160-6170.
- Keysar, S; Shter, G. E.; de Hazan, Y; Cohen, Y; Grader, G. S. *Chem. Mater.* **1997**, 9, 2464-2467.